Annals of Agricultural Science (2014) 59(2), 201–206

HOSTED BY

Faculty of Agriculture, Ain Shams University

Annals of Agricultural Science

www.elsevier.com/locate/aoas

^{1}H NMR spectral analysis as a new aspect to evaluate the stability of some edible oils

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Received 3 July 2014; accepted 10 July 2014

KEYWORDS

Stability;
^{1}H NMR spectroscopy;
Extra virgin olive oil;
Moringa oil:
apricot kernel oil;
Sunflower oil

Abstract Oxidative stability is one of the most important indicators for maintaining the quality of edible oils. ^{1}H NMR fingerprinting is used to evaluate the stability of edible oils at room temperature. The assignments of the ^{1}H NMR signals of the major and minor components of unoxidized edible oils and the oil stability prediction were given. Minor components of the oils are playing an essential role in defining oil authenticity and quality. Extra virgin olive oil (EVOO) showed β-sitosterol, whereas, moringa oil (MO) showed β-sitosterol and stigmasterol. MO showed nonglyceride fraction, aliphatic chains and olefins. Sunflower oil (SO) could be easily distinguished due to its high linoleic acid content followed by apricot kernel oil (AKO). The order of stability of edible oils under study was: MO > EVOO > AKO > SO. ^{1}H NMR spectral data agreed with the results obtained from Rancimat method for the determination of oxidative stability of edible oils under study. The main advantages of this method are the short time of analysis, the possibility to analyze samples without any preliminary treatment, and the small quantity of sample required.

Introduction

Nuclear magnetic resonance (NMR) can be applied to a wide range of liquid and solid matrices without altering the sample or producing hazardous wastes. NMR has several advantages relative to other common analytical tools such as high pressure liquid chromatography (HPLC), gas chromatography (GC) and mass spectrometry (MS). Topics covered include chemical compositional analysis and structural identification of functional components in foods, determination of composition and formulation of packaging materials, detection of food authentication, optimization of food processing parameters, and inspection of microbiological, physical and chemical quality of foods. Since 1993, NMR has become an AOCS Official Method to determine solid fat contents (SFC) of fats and oils in the food industry, particularly in the bakery, confectionery and margarine industries. Although several analytical methods already exist for the detection of virgin olive oil (VOO) adulteration, NMR fingerprinting was proven to be a much more effective method in the authentication of VOOs based on their geographical origin (Mannina et al., 2012; Dais and Hatzakis,

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Peer review under responsibility of Faculty of Agriculture, Ain-Shams University.

http://dx.doi.org/10.1016/j.aoas.2014.11.006
0570-1783

2013; Marcone et al., 2013). ^{1}H NMR has also been employed to estimate some physico-chemical analysis parameters in vegetable oils and their transesterificated products. Determination of the degree of unsaturation of combined and free fatty acids was found to be satisfactory when compared with the classical expression (Andrade et al., 2012). Determination of free fatty acids in pharmaceutical lipids by ^{1}H NMR and comparison with the classical acid value (AV) was achieved. Investigations showed that, for fatty oils, the NMR method was suitable to reproduce the results of the classical AV method (Skiera et al., 2014). Quantitative NMR analysis provided the fatty acid chain profiles of the total lipid extracts. The transesterification of the total lipid extracts furnished fatty acids methyl ester (FAME) mixtures that enabled quantitation of fatty acid acyl chains in the acylglycerol and free fatty acid (FFA) portions (Hatzakis et al., 2011; Siciliano et al., 2013).

^{1}H NMR has been demonstrated to be very useful in determining the composition in acyl groups of edible oils (Guillén and Uriarte, 2012a, 2012c; Sopelana et al., 2013; Martínez-Yusta and Guillén, 2014a, 2014b). This technique has also been employed to study other oil components that are usually present in much lower concentrations than triglycerides, such as mono- and di-glycerides and antioxidant compounds such as phytosterols and tocopherols (Alonso-Salces et al., 2010, 2011). The evolution of the molar percentage of several kinds of acyl groups of extra virgin olive, sunflower and virgin linseed oils was monitored throughout heating at frying temperature by means of ^{1}H NMR (Guillén and Uriarte, 2013). During heating of sunflower oil, the simultaneous monitoring of the iodine value (IV), acyl groups' proportions and aldehydes concentrations was carried out by ^{1}H NMR (Guillén and Uriarte, 2012b). Iodine values of the extracted oils were estimated by using the developed ^{1}H NMR spectroscopic method, which was correlated with the triglycerides (TG) content present in the sample determined by ^{1}H NMR (Kumar et al., 2011).

In a recent study simulating the adulteration of extra virgin olive oil with hazelnut oil, a low field 60 MHz ^{1}H NMR was used. There were qualitative differences between spectra from the two oil types. A single internal ratio of 2 isolated groups of peaks could detect hazelnut oil in extra virgin olive oil at the level of ~13% w/w, whereas a whole-spectrum chemometric approach brought the limit of detection down to 11.2% w/w for a set of independent test samples. When the ^{1}H NMR spectroscopy performance was compared to that of Fourier transform infrared (FTIR) spectroscopy, the ^{1}H NMR spectroscopy delivered comparable sensitivity and improved specificity, making it a superior screening tool (Parker et al., 2014).

The present work aimed at the application of ^{1}H NMR spectroscopy as a rapid, nondestructive, authenticity measuring tool to evaluate the stability of edible oils such as extra virgin olive, moringa, apricot kernel and sunflower oils.

Materials and methods

Materials

Fresh olive fruits *(Coratina olive variety of early ripe stage)* were brought during seasons of 2012 from Horticulture Research Institute Farm (Giza). Moringa seeds *(Moringa oleifera variety)* were brought during seasons of 2012 from Desert Research Center Farm in El-Sheikh Zowaid. Apricot kernels were brought during seasons of 2012 from Fruit Drying Factory in Food Technology Research Institute (Giza). Crude sunflower oil (SO) was obtained from Arma Oil Industries (Tenth of Ramadan City, Sharqia). All chemicals used were analytical grades.

Methods

EVOO was extracted from the fresh olive fruits by Oliomio-machine then filtered and kept in brown glass bottles at −5 °C till time of analysis. MO was extracted from moringa seeds by solvent (hexane). AKO was extracted from apricot kernels by solvent (hexane).

Instrumentation and spectral data acquisition

Oils samples under study were dissolved in dimethyl sulphoxide (DMSO) solvent for ^{1}H NMR Determination. ^{1}H NMR spectra were recorded on a Varian Gemini 300 BB NMR Spectrometer (USA) with Oxford 300 MHz NMR Magnet, Gemini 2000 Console and 5 mm probe, located at Main Chemical Laboratory in Ministry of Defense, Egypt. Observing ^{1}H at 300 MHz at temperature of 25 °C, ^{1}H NMR spectra were acquired using spectral width of 8000 Hz, relaxation delay of 1 s, 64 repetitions, acquisition time of 1.998 s and with a total time of 3 min, 37 s. Chemical shifts are expressed in δ units (ppm).

Results and discussion

Chemical shift assignments

In the spectrum, all hydrogen atoms having the same chemical surroundings produce signals at the same frequency. The position of a resonance signal in the spectrum is called the chemical shift and denoted as δ symbol. The chemical shift, the intensity and multiplicity of the resonance lines contain very useful information on each different type of ^{1}H nucleus in the sample. The chemical shift of an atom or a group of atoms is measured with respect to a reference compound which for ^{1}H is tetramethylsilane (TMS), its $\delta = 0.00$. The chemical shifts are obtained in parts per million (ppm) by dividing the frequency difference between the sample signals and the TMS signal, in hertz, by the TMS frequency in megahertz. For this reason, the chemical shift, in ppm, is independent of the measuring field strength, but the separation in hertz of two signals with a certain chemical shift difference increases linearly with field strength. Chemical shifts of lipid signals are always positive with respect to TMS and are characteristic of each particular molecular environment. Edible oils are mainly made up of triglycerides, with different substitution patterns due to length, degree and kind of unsaturation of the acyl groups, and minor components such as mono- and di-glycerides, sterols, vitamins, fatty acids, and others (Guillén and Ruiz, 2001).

Figs. 1–4 show the ^{1}H NMR spectra of pure extra virgin olive, moringa, apricot kernel and sunflower oils acquired at 300 MHz.

Tables 1–4 summarize the chemical shift assignments of the ^{1}H NMR signals of the main components of oils under investigations.

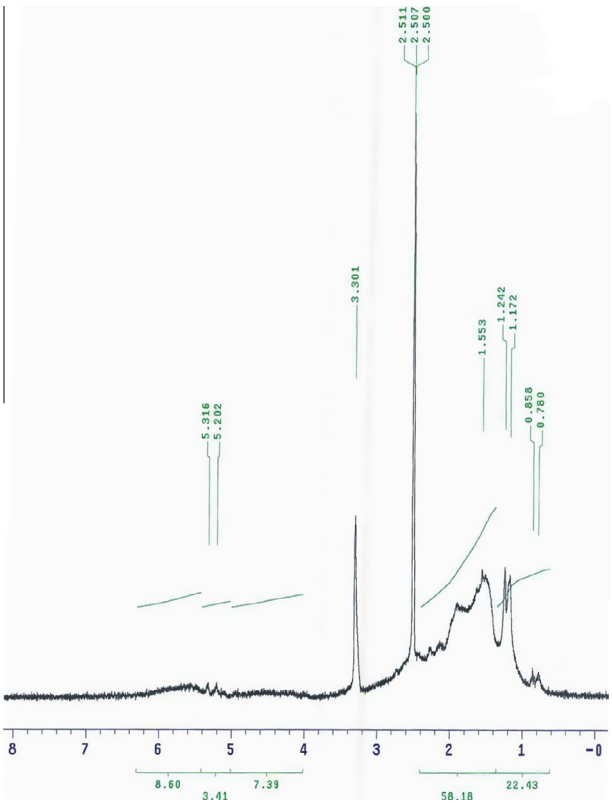

Fig. 1 Typical [1]H NMR spectra of pure EVOO.

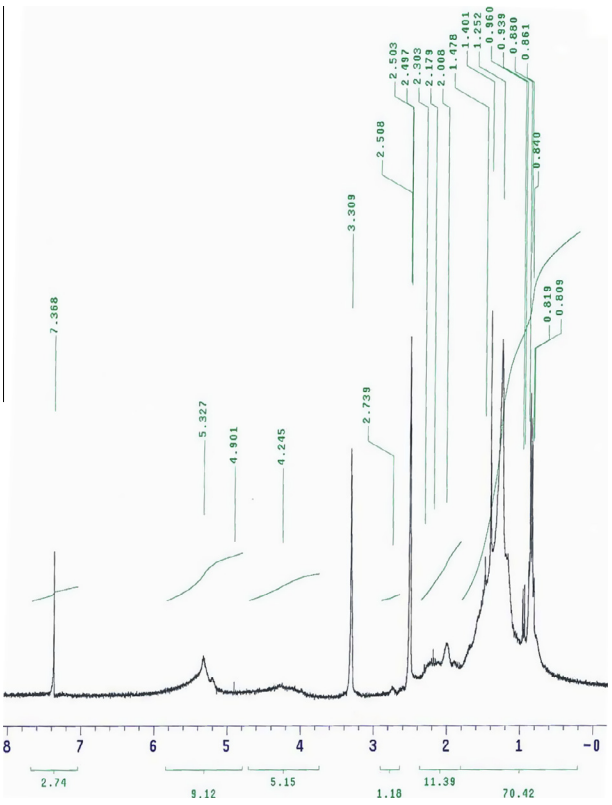

Fig. 3 Typical [1]H NMR spectra of pure AKO.

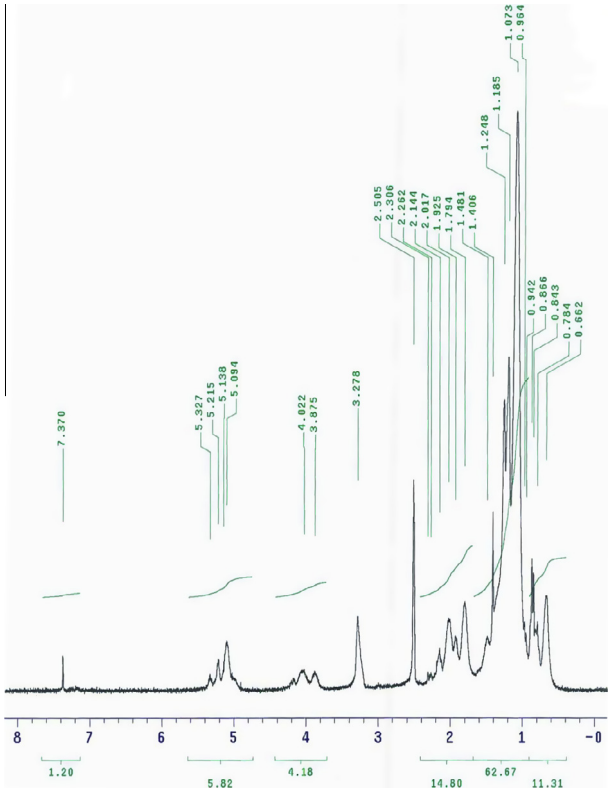

Fig. 2 Typical [1]H NMR spectra of pure MO.

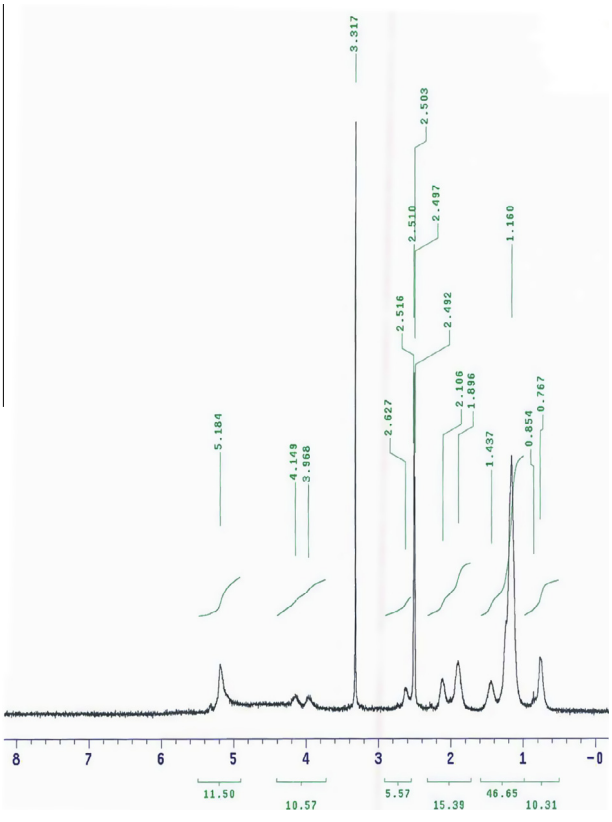

Fig. 4 Typical [1]H NMR spectra of pure SO.

Table 1 Chemical shift (δ) assignments of the ^{1}H NMR signals of the main components of EVOO.

δ (ppm)	Functional group	Attribution
0.780	—CH_3 (C18-steroid group)	β-sitosterol
0.858	—CH_3 (acyl group)	Sat., oleic and linoleic
1.172	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.242	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.553	—OCO—CH_2—CH_2— (acyl group)	Oleyl acyl chains
2.500	DMSO	Solvent DMSO
2.507	DMSO	Solvent DMSO
2.511	DMSO	Solvent DMSO
3.301	DMSO	H_2O of DMSO
5.202	>CHOCOR (glyceryl group)	Triglycerides
5.316	—CH=CH— (acyl group)	Unsaturated fatty acids

Table 2 Chemical shift (δ) assignments of the ^{1}H NMR signals of the main components of MO.

δ (ppm)	Functional group	Attribution
0.662	—CH_3 (C18-steroid group)	Stigmasterol
0.784	—CH_3 (C18-steroid group)	β-sitosterol
0.843	—CH_3 (acyl group)	Sat., oleic and linoleic
0.866	—CH_3 (acyl group)	Sat., oleic and linoleic
0.942	—CH_3 (acyl group)	Sat., oleic and linoleic
0.964	—CH_3 (acyl group)	Sat., oleic and linoleic
1.073	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.185	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.248	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.406	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.481	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.794	>C=C—CH_3 (allylic group)	Allyl chain
1.925	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.017	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.144	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.262	—OCO—CH_2— (acyl group)	Oleyl acyl chains
2.306	—OCO—CH_2— (acyl group)	Oleyl acyl chains
2.505	DMSO	Solvent DMSO
3.278	DMSO	H_2O of DMSO
3.875	—CH_2OH (glyceryl group)	*sn*-1,2 Diacylglycerol
4.022	>CH—OH	*sn*-1,3 Diacylglycerol
5.094	—CH_2—O—CO—R	*sn*-1,3 Diacylglycerol
5.138	>CHOCOR (glyceryl group)	Triglycerides
5.215	>CHOCOR (glyceryl group)	Triglycerides
5.327	—CH=CH— (acyl group)	Unsaturated fatty acids
7.370	—CH=CH— (olefinic protons)	Olefins

Table 3 Chemical shift (δ) assignments of the ^{1}H NMR signals of the main components of AKO.

δ (ppm)	Functional group	Attribution
0.809	—CH_3 (acyl group)	Sat., oleic and linoleic
0.819	—CH_3 (acyl group)	Sat., oleic and linoleic
0.840	—CH_3 (acyl group)	Sat., oleic and linoleic
0.861	—CH_3 (acyl group)	Sat., oleic and linoleic
0.880	—CH_3 (acyl group)	Sat., oleic and linoleic
0.939	—CH_3 (acyl group)	Sat., oleic and linoleic
0.960	—CH_3 (acyl group)	Linolenic
1.252	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.401	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.478	—$(CH_2)_n$— (acyl group)	Aliphatic chains
2.008	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.179	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.303	—OCO—CH_2— (acyl group)	Oleyl acyl chains
2.497	DMSO	Solvent DMSO
2.503	DMSO	Solvent DMSO
2.508	DMSO	Solvent DMSO
2.739	=CH—CH_2—CH= (acyl group)	Poly unsaturated fatty acids
3.309	DMSO	H_2O of DMSO
4.245	—CH_2OCOR (glyceryl group)	*sn*-1,3 Diacylglycerol
4.901	—CH_2OCOR (glyceryl group)	*sn*-1,3 Diacylglycerol
5.327	—CH=CH— (acyl group)	Unsaturated fatty acids
7.368	—CH=CH— (olefinic protons)	Olefins

Table 4 Chemical shift (δ) assignments of the ^{1}H NMR signals of the main components of SO.

δ (ppm)	Functional group	Attribution
0.767	—CH_3 (acyl group)	Sat., oleic and linoleic
0.854	—CH_3 (acyl group)	Sat., oleic and linoleic
1.160	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.437	—$(CH_2)_n$— (acyl group)	Aliphatic chains
1.896	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.106	—CH_2—CH=CH— (acyl group)	Unsaturated fatty acids
2.492	—OCO—CH_2— (acyl group)	Oleyl acyl chains
2.497	—OCO—CH_2— (acyl group)	Oleyl acyl chains
2.503	DMSO	Solvent DMSO
2.510	DMSO	Solvent DMSO
2.516	DMSO	Solvent DMSO
2.627	—CH_3 (acyl group)	Linoleic
3.317	DMSO	H_2O of DMSO
3.968	—CH_2OH (glyceryl group)	*sn*-1,2 Diacylglycerol
4.149	—CH_2OCOR (glyceryl group)	*sn*-1,3 Diacylglycerol
5.184	—CH=CH— (acyl group)	Unsaturated fatty acids

From the Figs. 1–4, it was noticed the apparent differences between the ^{1}H NMR spectra of different edible oils (EVOO, MO, AKO, SO). These differences help in the identification and authentication of each edible oil as its ^{1}H NMR fingerprint.

^{1}H NMR signals of hydroperoxides (primary oxidation products) and aldehydes (main secondary oxidation products) were not detected in the edible oils under this study indicating that no oxidative degradation was taking place. The presence of these oxidation products in the ranges 8.09–8.19 ppm for hydroperoxides proton, and 9.30–9.90 ppm for aldehydes, indicates oxidation of these edible oils (Alonso-Salces et al., 2011).

From an authenticity point of view, the most interesting ^{1}H signals are likely to be those of the methyl groups. The methyl groups of the linolenic acyl chains (methyl groups of n-3 fatty acids) appear slightly different to the methyl groups of the other fatty acid chains. Because these vegetable oils contain less linolenic acid than others, it is possible to use this information to discriminate among these oils. Also, a ^{1}H NMR spectrum of an edible oil shows the signals corresponding to the major components in the oil. The presence of some other components may be detected by analyzing the small signals that appeared in the baseline. Because oil stability varies from one oil to another and depends on its triacylglycerol composition as well as the presence of different minor components in the oils, different attempts have been carried out to quantify

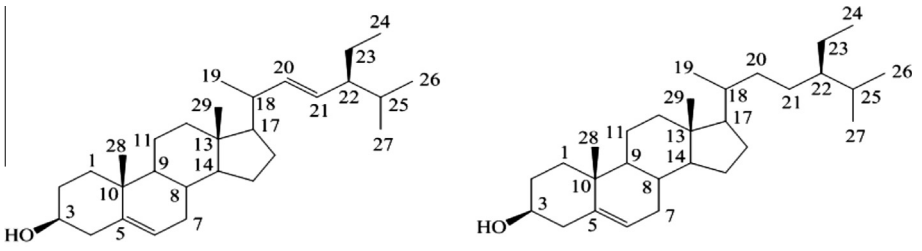

Fig. 5 The chemical structures of stigmasterol (1) and β-sitosterol (2).

these components in the oils and to correlate these results with the stability of the corresponding oils. Among all these signals, some of the most interesting are these corresponding volatile compounds (Hidalgo and Zamora, 2003).

SO could be easily distinguished from the other edible oils under investigations due to its high linoleic acid content that is particularly evident in the intensity of the signal resonating at 2.627 ppm. Protons of linoleic acid give visible signals at 0.854 ppm, and at 2.106 ppm, due, respectively, to the terminal methyl group and to the allylic protons of linoleic acid. Linolenic acid contains two inner allylic methylene groups (—CH═CH—CH_2—CH═CH—CH_2—CH═CH—).

[1]H NMR spectra of edible oils under investigation showed DMSO solvent peaks as 2 apparent peaks slightly different in chemical shifts ranging between 3.317 and 3.278 ppm for the first peak and ranging between 2.500 and 2.497 for the second peak, as following peaks which are singlet at 3.301 ppm and triplet at 2.511, 2.507, 2.500 ppm for EVOO, singlet at 3.278 ppm and singlet at 2.505 ppm for MO, singlet at 3.309 ppm and triplet at 2.508, 2.503, 2.497 ppm for AKO, and singlet at 3.317 ppm and sextet at 2.627, 2.516, 2.510, 2.503, 2.497, 2.492 ppm for SO. We notice that the less chemical shift corresponds to MO then EVOO then AKO then SO in the last. This order may reflect the stability order of these edible oils and agrees with results from determination of oxidative stability by Rancimat method where the order of stability was MO > EVOO and comes in an excellent agreement with the order of tocopherols concentrations as powerful natural antioxidants (Tsaknis et al., 1999).

Glycerol and unsaturated protons for all oils appeared between 4.10 and 5.40 ppm, whereas, saturated protons signals appeared between 0.80 and 2.80 ppm. Proton signals of the methylene group directly adjacent to the carbonyl group of fatty acids (α-carbonyl-CH_2) resonating at 2.2–2.4 ppm were found only in MO and AKO. For MO, the allylic and olefinic protons, owing to oleic, linoleic and linolenic groups, in relation to that of methylene protons in the α-position in relation to the carbonyl group could be observed at 1.794 ppm for allylic protons ≻C═C—CH_3, and at 7.370 ppm for olefinic protons. MO and AKO also had apparent proportions of olefinic protons resonating at 7.3 ppm. It was noticed that AKO had higher proportion of olefinic protons than MO.

AKO had apparent linoleic acid content that is particularly evident in the intensity of the signal resonating at 2.739 ppm.

For EVOO, a major peak at 1.553 ppm with a considerable intensity of 58.18% characterizes EVOO assigned to —OCO—CH_2—CH_2— (oleyl acyl chains), a peak at 5.202 ppm assigned to ≻CHOCOR (glyceryl groups), a peak at 5.316 ppm assigned to —CH═CH— (acyl groups), a peak at 0.858 ppm, assigned to —CH_3 (saturated, oleic and linoleic acyl groups), a peak at 0.780 ppm assigned to methyl protons, 2 peaks at 1.242, 1.172 ppm assigned to methylene protons of —$(CH_2)_n$— (acyl groups) were observed.

The presence of sterols in MO could be deduced from the signals between 0.470 and 0.784 ppm due to methylic protons in position C18 of the steroidal skeleton. Sterols appeared near the more intense signal of the methyl protons of the fatty acids [—CH_3 (C18-steroid group)] as shown clearly in the right-hand side inset of Fig. 2.

EVOO showed a peak at 0.780 ppm assigned to β-sitosterol. Whereas, MO showed both β-sitosterol and stigmasterol at 0.784, 0.662 ppm, respectively. These signals were attributed to the methyl protons of all sterols at position 18. Fig. 5 shows the chemical structures of stigmasterol (1) and β-sitosterol (2). It has been suggested that a donation of hydrogen atom from the allylic methyl group in the side chain, followed by the isomerization to a relatively tertiary allylic free radical responded the mode of action of the sterol antioxidants. MO was the most rich in the aliphatic chains. Although EVOO and MO had high oleic acid content, in addition, EVOO contained linoleic and linolenic acids, which were contained in much lower quantity in MO and which more readily undergoes oxidation and degradation than oleic acid. The long induction period of MO might be explained by the presence of sterols. However, EVOO, which had a shorter induction period, had a higher content of those sterols. Furthermore, the higher oxidative stability of MO over EVOO should be attributed to other constituents of the non glyceride fraction of the oil, which possess antioxidant properties. Olefins might be responsible for higher stability of MO since olefins bear an incidental relationship to antioxidants (Tsaknis et al., 1999).

Conclusions

[1]H NMR spectroscopy is a very useful technique in the study of several aspects of edible oils and fats. It has the advantages that it is not destructive, requires a very small sample whose preparation is very simple, and it takes short time. A single run detects all the protons present in the sample and provides signals whose intensities reflect the proportions of protons with the same local field, or in other words, with the same chemical environment. So this technique enables the evaluation of both the major components of the sample and also of some minor components if their concentration is enough to be detected and if their signals do not overlap with those of the main

components. Library searching in the ^{1}H NMR region is a well established and powerful way which was used in comparison and matching of measured spectra.

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